

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 167 567 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

02.01.2002 Bulletin 2002/01

(51) Int Cl.7: C23C 16/02

(21) Application number: 01304779.0

(22) Date of filing: 31.05.2001

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 28.06.2000 US 605593

03.10.2000 US 678266

(71) Applicant: Applied Materials, Inc.
Santa Clara, California 95054 (US)

(72) Inventors:

- Xi, Ming
Milpitas, CA 95035 (US)
- Sinha, Ashok
Palo Alto, CA 94306 (US)
- Kori, Moris
Palo Alto, CA 94301 (US)

- Mak, Alfred W.
Union City, CA 94587 (US)
- Byun, Jeong Soo
Cupertino, CA 95014 (US)
- Chung-Lai Lei, Lawrence
Milpitas, CA 95035 (US)
- Chung, Hua
San Jose, CA 95129 (US)
- Lu, Xinliang
Sunnyvale, CA 94086 (US)
- Lai, Ken Kaung
Milpitas, CA 95035 (US)
- Littau, Karl A.
Palo Alto, CA 94303 (US)

(74) Representative: Allard, Susan Joyce et al
BOULT WADE TENNANT, Verulam Gardens 70
Gray's Inn Road
London WC1X 8BT (GB)

(54) Method and apparatus for depositing refractory metal layers employing sequential deposition techniques to form a nucleation layer

(57) A method and system to form a refractory metal layer on a substrate features nucleating a substrate using sequential deposition techniques in which the substrate is serially exposed to first and second reactive gases followed by forming a layer, employing vapor deposition, to subject the nucleation layer to a bulk deposition of a compound contained in one of the first and second reactive gases. The process may be carried-out where all process steps occur in a common chamber or may occur in different chambers. For example, nucleation may be carried-out in a processing chamber that is different from the processing chamber in which the bulk deposition occurs. Also disclosed is a technique for controlling the presence of fluorine atoms in the resulting layer as a function of the carrier gas employed during nucleation.

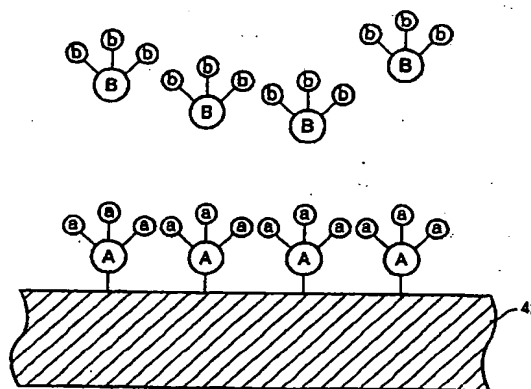


FIG. 3

EP 1 167 567 A1

Description

[0001] This invention relates to the processing of semiconductor substrates. More particularly, this invention relates to improvements in the process of depositing refractory metal layers on semiconductor substrates.

[0002] The semiconductor processing industry continues to strive for larger production yields while increasing the uniformity of layers deposited on substrates having larger surface areas. These same factors in combination with new materials also provide higher integration of circuits per unit area of the substrate. As circuit integration increases, the need for greater uniformity and process control regarding layer thickness rises. As a result, various technologies have been developed to deposit layers on substrates in a cost-effective manner, while maintaining control over the characteristics of the layer. Chemical Vapor Deposition (CVD) is one of the most common deposition processes employed for depositing layers on a substrate. CVD is a flux-dependent deposition technique that requires precise control of the substrate temperature and precursors introduced into the processing chamber in order to produce a desired layer of uniform thickness. These requirements become more critical as substrate size increases, creating a need for more complexity in chamber design and gas flow technique to maintain adequate uniformity.

[0003] A variant of CVD that demonstrates superior step coverage compared to CVD, is Atomic Layer Deposition (ALD). ALD is based upon Atomic Layer Epitaxy (ALE) that was employed originally to fabricate electroluminescent displays. ALD employs chemisorption to deposit a saturated monolayer of reactive precursor molecules on a substrate surface. This is achieved by alternately pulsing an appropriate reactive precursor into a deposition chamber. Each injection of a reactive precursor is separated by an inert gas purge to provide a new atomic layer additive to previously deposited layers to form a uniform layer on the substrate. The cycle is repeated to form the layer to a desired thickness. A drawback with ALD techniques is that the deposition rate is much lower than typical CVD techniques by at least one order of magnitude.

[0004] Formation of film layers at a high deposition rate while providing adequate step coverage are conflicting characteristics often necessitating sacrificing one to obtain the other. This conflict is true particularly when refractory metal layers are deposited to cover gaps or vias during formation of contacts that interconnect adjacent metallic layers separated by dielectric layers. Historically, CVD techniques have been employed to deposit conductive material such as refractory metals in order to inexpensively and quickly form contacts. Due to the increasing integration of semiconductor circuitry, tungsten has been used based upon superior step coverage. As a result, deposition of tungsten employing CVD techniques enjoys wide application in semiconductor processing due to the high throughput of the process.

[0005] Depositing tungsten by traditional CVD methods, however, is attendant with several disadvantages. For example, blanket deposition of a tungsten layer on a semiconductor wafer is time-consuming at temperatures below 400° C. The deposition rate of tungsten may be improved by increasing the deposition temperature to, e.g., about 500° C to about 550° C; however, temperatures in this higher range may compromise the structural and operational integrity of the underlying portions of the integrated circuit being formed. Use of tungsten has also frustrated photolithography steps during the manufacturing process as it results in a relatively rough surface having a reflectivity of 20% or less than that of a silicon substrate. Finally, tungsten has proven difficult to deposit uniformly. Variance in film thickness of greater than 1% has been shown with tungsten, thereby frustrating control of the resistivity of the layer. Several prior attempts to overcome the aforementioned drawbacks have been attempted.

[0006] For example, in United States patent number 5,028,565 to Chang et al., which is assigned to the assignee of the present invention, a method is disclosed to improve, *inter alia*, uniformity of tungsten layers by varying the deposition chemistry. The method includes, in pertinent part, formation of a nucleation layer over an intermediate barrier layer before depositing the tungsten layer via bulk deposition. The nucleation layer is formed from a gaseous mixture of tungsten hexafluoride, hydrogen, silane and argon. The nucleation layer is described as providing a layer of growth sites to promote uniform deposition of a tungsten layer thereon. The benefits provided by the nucleation layer are described as being dependent upon the barrier layer present. For example, were the barrier layer formed from titanium nitride, the tungsten layer's thickness uniformity is improved as much as 15%. Were the barrier layer formed from sputtered tungsten or sputtered titanium tungsten, the benefits provided by the nucleation layer are not as pronounced.

[0007] A need exists, therefore, to provide techniques to improve the characteristics of refractory metal layers deposited on semiconductor substrates.

[0008] A method and system to form a refractory metal layer on a substrate features nucleating a substrate using sequential deposition techniques in which the substrate is serially exposed to first and second reactive gases followed by forming a layer, employing vapor deposition, to subject the nucleation layer to a bulk deposition of a compound contained in one of the first and second reactive gases. The process may be carried-out where all process steps occur in a common chamber or may occur in different chambers. For example, nucleation may be carried-out in a processing chamber that is different from the processing chamber in which the bulk deposition occurs. Also disclosed is a technique for controlling the presence of fluorine atoms in the resulting layer as a function of the carrier gas employed during nucleation.

[0009] The following drawings are provided by way of example:

Fig. 1 is a perspective view of a semiconductor processing system in accordance with the present invention;

Fig. 2 is a detailed view of the processing chambers shown above in Fig. 1;

Fig. 3 is a schematic view showing deposition of a first molecule onto a substrate during sequential deposition;

Fig. 4 is a schematic view showing deposition of second molecule onto a substrate during sequential deposition to form a refractory metal layer;

Fig. 5 is a graphical representation showing the concentration of gases, introduced into the processing chamber shown above in Fig. 2, and the time in which the gases are present in the processing chamber, in accordance with the present invention;

Fig. 6 is a graphical representation showing the relationship between the number of ALD cycles and the thickness of a layer formed on a substrate employing sequential deposition techniques, in accordance with the present invention;

Fig. 7 is a graphical representation showing the relationship between the number of sequential deposition cycles and the resistivity of a layer formed on a substrate employing sequential deposition techniques, in accordance with the present invention;

Fig. 8 is a graphical representation showing the relationship between the deposition rate of a layer formed on a substrate employing sequential deposition techniques and the temperature of the substrate;

Fig. 9 is a graphical representation showing the relationship between the resistivity of a layer formed on a substrate employing sequential deposition techniques and the temperature of the substrate, in accordance with the present invention;

Fig. 10 is a cross-sectional view of a patterned substrate having a nucleation layer formed thereon employing sequential deposition techniques, in accordance with the present invention;

Fig. 11 is a partial cross-sectional view of the substrate, shown above in Fig. 10, with a refractory metal layer formed atop of the nucleation layer employing CVD, in accordance with the present inven-

tion;

Fig. 12 is a graphical representation showing the concentration of gases shown above in Fig. 3 in accordance with a first alternate embodiment of the present invention;

Fig. 13 is a graphical representation showing the concentration of gases shown above in Fig. 5 in accordance with a second alternate embodiment of the present invention;

Fig. 14 is a graphical representation showing the fluorine content versus depth of a refractory metal layer formed on a substrate employing ALD either Ar or N₂ being a carrier gas; and

Fig. 15 is a graphical representation showing the fluorine content versus depth of a refractory metal layer formed on a substrate employing ALD with H₂ being a carrier gas.

[0010] Referring to Fig. 1, an exemplary wafer processing system includes one or more processing chambers 12 and 14 disposed in a common work area 16 surrounded by a wall 18. Processing chambers 12 and 14 are in data communication with a controller 22 that is connected to one or more monitors, shown as 24 and 26. The monitors typically display common information concerning the process associated with processing chambers 12 and 14. One of the monitors 26 is mounted to wall 18, with the remaining monitor 24 being disposed in work area 16. Operational control of processing chambers 12 and 14 may be achieved by the use of a light pen, associated with one of the monitors 24 and 26, to communicate with controller 22. For example, light pen 28 is associated with monitor 24 and facilitates communication with controller 22 through monitor 24. Light pen 39 facilitates communication with controller 22 through monitor 26.

[0011] Referring both to Figs. 1 and 2, each of processing chambers 12 and 14 includes a housing 30 having a base wall 32, a cover 34, disposed opposite to base wall 32, and a sidewall 36, extending therebetween. Housing 30 defines a chamber 37, and a pedestal 38 is disposed within processing chamber 37 to support a substrate 42, such as a semiconductor wafer. Pedestal 38 may be mounted to move between cover 34 and base wall 32, using a displacement mechanism (not shown), but the position thereof is typically fixed. Supplies of processing gases 39a, 39b and 39c are in fluid communication with processing chamber 37 via a showerhead 40. Regulation of the flow of gases from supplies 39a, 39b and 39c is effectuated via flow valves 41.

[0012] Depending on the specific process, substrate 42 may be heated to a desired temperature prior to layer deposition via a heater embedded within pedestal 38.

For example, pedestal 38 may be resistively heated by applying an electric current from AC power supply 43 to heater element 44. Substrate 42 is, in turn, heated by pedestal 38, and can be maintained within a desired process temperature range of, for example, about 20 °C to about 750 °C. A temperature sensor 46, such as a thermocouple, is also embedded in wafer support pedestal 38 to monitor the temperature of pedestal 38 in a conventional manner. For example, the measured temperature may be used in a feedback loop to control the electrical current applied to heater element 44 by power supply 43 such that the substrate temperature can be maintained or controlled at a desired temperature that is suitable for the particular process application. Optionally, pedestal 38 may be heated using radiant heat (not shown). A vacuum pump 48 is used to evacuate processing chamber 37 and to help maintain the proper gas flows and pressure inside processing chamber 37.

[0013] Referring to Figs. 1 and 3, one or both of processing chambers 12 and 14, discussed above may operate to deposit refractory metal layers on the substrate employing sequential deposition techniques. One example of sequential deposition techniques in accordance with the present invention includes atomic layer deposition (ALD). Depending on the specific stage of processing, the refractory metal layer may be deposited on the material from which substrate 42 is fabricated, e.g. SiO₂. The refractory metal layer may also be deposited on a layer previously formed on substrate 42, e.g., titanium, titanium nitride and the like.

[0014] During the sequential deposition technique in accordance with the present invention, a batch of a first processing gas, in this case Aa_x, results in a layer of A being deposited on substrate 42 having a surface of ligand and a exposed to processing chamber 37. Thereafter, a purge gas enters processing chamber 37 to purge gas Aa_x, which has not been incorporated into the layer of A. After purging gas Aa_x from processing chamber 37, a second batch of processing gas, Bb_y, is introduced into processing chamber 37. The a ligand present on the substrate surface reacts with the b ligand and B atom, releasing molecules, for example, ab and aA, which move away from substrate 42 and are subsequently pumped from processing chamber 37. In this manner, a surface comprising a layer of B compound remains upon substrate 42 and exposed to processing chamber 37, shown in Fig. 4. The composition of the layer of B compound may be a monolayer of atoms typically formed employing ALD techniques. Alternatively, the layer of compound B may include a layer of multiple atoms. In such a case, the first processing gases may include a mixture of process gases, each of which has atoms that would adhere to substrate 42. The process proceeds cycle after cycle, until the desired thickness is achieved.

[0015] Referring to both Figs. 2 and 5, although any type of processing gas may be employed, in the present example, the processing gas Aa_x includes B₂H₆ and the processing gas Bb_y is WF₆. Two purge gases are em-

ployed: Ar and N₂. Each of the processing gases was flowed into processing chamber 37 with a carrier gas, which in this example were one of the purge gases: WF₆ is introduced with Ar and B₂H₆ is introduced with N₂. It should be understood, however, that the purge gas may differ from the carrier gas, discussed more fully below. One cycle of the ALD technique in accordance with the present invention includes flowing the purge gas, N₂, into processing chamber 37 during time t₁, which is approximately 0.01 to 15 seconds before B₂H₆ is flowed into processing chamber 37. During time t₂, the processing gas B₂H₆ is flowed into processing chamber 37 for a time in the range of 0.01 to 15 seconds, along with a carrier gas, which in this example is N₂. After 0.01 to 15 seconds have lapsed, the flow of B₂H₆ terminates and the flow of N₂ continues during time t₃ for an additional time in the range of 0.01 to 15 seconds, purging the processing chamber of B₂H₆. During time t₄, processing chamber 37 is pumped so as to remove most, if not all, gases. After pumping of process chamber 37, the carrier gas Ar is introduced for a time in the range of 0.01 to 15 seconds during time t₅, after which time the process gas WF₆ is introduced into processing chamber 37, along with the carrier gas Ar during time t₆. The time t₆ lasts between 0.01 to 15 seconds. The flow of the processing gas WF₆ into processing chamber 37 is terminated approximately 0.01 to 15 seconds after it commenced. After the flow of WF₆ into processing chamber 37 terminates, the flow of Ar continues for an additional time in the range of 0.01 to 15 seconds, during time t₇. Thereafter, processing chamber 37 is pumped so as to remove most, if not all, gases therein, during time t₈. As before, the pumping process lasts approximately thirty seconds, thereby concluding one cycle of the sequential deposition technique in accordance with the present invention.

[0016] The benefits of employing the sequential deposition technique are manifold, including flux-independence of layer formation that provides uniformity of deposition independent of the size of a substrate. For example, the measured difference of the layer uniformity and thickness measured between a 200 mm substrate and a 32 mm substrate deposited in the same chamber is negligible. This is due to the self-limiting characteristics of the sequential deposition techniques. Further, this technique contributes to a near-perfect step coverage over complex topography.

[0017] In addition, the thickness of the layer B, shown in Fig. 4, may be easily controlled while minimizing the resistance of the same by employing sequential deposition techniques. With reference to Fig. 6 it is seen in the slope of line 50 that the thickness of the tungsten layer B is proportional to the number of cycles employed to form the same. The resistivity of the tungsten layer, however, is relatively independent of the thickness of the layer, as shown by the slope of line 52 in Fig. 7. Thus, employing sequential deposition techniques, the thickness of a refractory metal layer may be easily controlled

as a function of the cycling of the process gases introduced into the processing chamber with a negligible effect on the resistivity.

[0018] Referring to both Figs. 4 and 8, control of the deposition rate was found to be dependent upon the temperature of substrate 42. As shown by the slope of line 54, increasing the temperature of substrate 42 increased the deposition rate of the tungsten layer B. For example, at 56, the deposition rate is shown to be approximately 2 Å/cycle at 250° C. However at point 58 the deposition rate is approximately 5 Å/cycle at a temperature of 450° C. The resistivity of the tungsten layer, however, is virtually independent of the layer thickness, as shown by the slope of curve 59, shown in Fig. 9. As a result, the deposition rate of the tungsten layer may be controlled as a function of temperature without compromising the resistivity of the same. However, it may be desired to reduce the time necessary to deposit an entire layer of a refractory metal.

[0019] To that end, a bulk deposition of the refractory metal layer may be included in the deposition process. Typically, the bulk deposition of the refractory metal occurs after the nucleation layer is formed in a common processing chamber. Specifically, in the present example, nucleation of a tungsten layer occurs in chamber 12 employing the sequential deposition techniques discussed above, with substrate 42 being heated in the range of 200° C to 400° C, and processing chamber 37 being pressurized in the range of 1 to 10 Torr. A nucleation layer 60 of approximately 12 to 20 nm is formed on a patterned substrate 42, shown in Fig. 10. As shown, substrate 42 includes a barrier layer 61 and a patterned layer having a plurality of vias 63. The nucleation layer is formed adjacent to the patterned layer covering vias 63. As shown, forming nucleation layer 60 employing ALD techniques provides 100% step coverage. To decrease the time required to form a complete layer of tungsten, a bulk deposition of tungsten onto nucleation layer 60 occurs using CVD techniques, while substrate 42 is disposed in the same processing chamber 12, shown in Fig. 1. The bulk deposition may be performed using recipes well known in the art. In this manner, a tungsten layer 65 providing a complete plug fill is achieved on the patterned layer with vias having aspect ratios of approximately 6:1, shown in Fig. 11.

[0020] In an alternative embodiment, a bifurcated deposition process may be practiced in which nucleation of the refractory metal layer occurs in a chamber that is different from the chamber in which the remaining portion of the refractory metal layer is formed. Specifically, in the present example, nucleation of a tungsten layer occurs in chamber 12 employing the sequential deposition techniques, such as ALD, discussed above. To that end, substrate 42 is heated in the range of 200° C to 400° C and chamber 37 is pressurized in the range of 1 to 10 Torr. A nucleation layer 60 of approximately 12 to 20 nm is formed on a patterned substrate 42, shown in Fig. 10. As shown, substrate 42 includes a bar-

rier layer 61 and a patterned layer having a plurality of vias 63. The nucleation layer is formed adjacent to the patterned layer covering the vias 63. As shown, forming the nucleation layer 60 employing sequential deposition techniques provides 100% step coverage.

[0021] Employing CVD techniques, bulk deposition of tungsten onto nucleation layer 60 occurs while substrate 42 is disposed in processing chamber 14, shown in Fig. 1. The bulk deposition may be performed using recipes well known in the art. In this manner, a tungsten layer 65 providing a complete plug fill is achieved on the patterned layer with vias having aspect ratios of approximately 6:1, shown in Fig. 11. Implementing the bifurcated deposition process discussed above may decrease the time required to form a tungsten layer having improved characteristics.

[0022] As mentioned above, in an alternate embodiment of the present invention, the carrier gas may differ from the purge gas, as shown in Fig. 12. The purge gas, which is introduced at time intervals t_1 , t_3 , t_5 and t_7 comprises Ar. The carrier gas, which is introduced at time intervals t_2 and t_6 , comprises of N_2 . Thus, at time interval t_2 the gases introduced into the processing chamber include a mixture of B_2H_6 and N_2 , and at time interval t_6 , the gas mixture includes WF_6 and N_2 . The pump process during time intervals t_4 and t_8 is identical to the pump process discussed above with respect to Fig. 5. In yet another embodiment, shown in Fig. 13, the carrier gas during time intervals t_2 and t_6 comprises H_2 , with the purge gas introduced at time intervals t_1 , t_3 , t_5 and t_7 comprising of Ar. The pump processes at time intervals t_4 and t_8 are as discussed above. As a result, at time interval t_2 the gas mixture introduced into processing chamber 37 consists of B_2H_6 and H_2 , and WF_6 and H_2 at time interval t_6 .

[0023] An advantage realized by employing the H_2 carrier gas is that the stability of the tungsten layer B may be improved. Specifically, by comparing curve 66 in Fig. 14 with curve 68 in Fig. 15, it is seen that the concentration of fluorine in the nucleation layer 60, shown in Fig. 10, is much less when H_2 is employed as the carrier gas, as compared with use of N_2 or Ar as a carrier gas.

[0024] Referring to both Figs. 14 and 15, the apex and nadir of curve 66 show that the fluorine concentration reaches levels in excess of 1×10^{21} atoms per cubic centimeter and only as low as just below 1×10^{19} atoms per cubic centimeter. Curve 68, however, shows that the fluorine concentration is well below 1×10^{21} atoms per cubic centimeter at the apex and well below 1×10^{17} atoms per cubic centimeter at the nadir. Thus, employing H_2 as the carrier gas provides a much more stable film, i. e., the probability of fluorine diffusing into the substrate, or adjacent layer is reduced. This also reduces the resistance of the refractory metal layer by avoiding the formation of a metal fluoride that may result from the increased fluorine concentration. Thus, the stability of the nucleation layer, as well as the resistivity of the same,

may be controlled as a function of the carrier gas employed. This is also true when a refractory metal layer is deposited entirely employing ALD techniques, i.e., without using other deposition techniques, such as CVD.

[0025] Referring again to Fig. 2, the process for depositing the tungsten layer may be controlled using a computer program product that is executed by controller 22. To that end, controller 22 includes a central processing unit (CPU) 70, a volatile memory, such as a random access memory (RAM) 72 and permanent storage media, such as a floppy disk drive for use with a floppy diskette, or hard disk drive 74. The computer program code can be written in any conventional computer readable programming language; for example, 68000 assembly language, C, C++, Pascal, Fortran and the like. Suitable program code is entered into a single file, or multiple files, using a conventional text editor and stored or embodied in a computer-readable medium, such as hard disk drive 74. If the entered code text is in a high level language, the code is compiled and the resultant compiler code is then linked with an object code of precompiled Windows® library routines. To execute the linked and, compiled object code the system user invokes the object code, causing the CPU 70 to load the code in RAM 72. The CPU 70 then reads and executes the code to perform the tasks identified in the program.

[0026] Although the invention has been described in terms of specific embodiments, one skilled in the art will recognize that various changes to the reaction conditions, i.e., temperature, pressure, film thickness and the like can be substituted and are meant to be included herein. Additionally, while the bifurcated deposition process has been described as occurring in a common system, the bulk deposition may occur in a processing chamber of a mainframe deposition system that is different from the mainframe deposition system in which the processing chamber is located that is employed to deposit the nucleation layer. Finally, other refractory metals may be deposited, in addition to tungsten, and other deposition techniques may be employed in lieu of CVD. For example, physical vapor deposition (PVD) techniques, or a combination of both CVD and PVD techniques may be employed. The scope of the invention should not be based upon the foregoing description. Rather, the scope of the invention should be determined based upon the claims recited herein, including the full scope of equivalents thereof.

Claims

1. A method for forming a layer on a substrate disposed in a processing chamber, said method comprising:

forming a nucleation layer by serially exposing said substrate to first and second reactive gas-

es; and

forming, atop of said nucleation layer, a bulk deposition layer employing vapor deposition to subject said nucleation layer to a bulk deposition of a compound contained in one of said first and second reactive gases.

2. The method as claimed in claim 1, wherein forming said nucleation layer and forming said bulk deposition layer occurs in a common processing chamber.
3. The method as claimed in claim 1, further including providing first and second processing chambers and placing said substrate in said first processing chamber before forming said nucleation layer and placing said substrate in said second processing chamber before forming said bulk deposition layer, wherein forming said nucleation layer occurs in said first processing chamber and forming said bulk deposition layer occurs in said second processing chamber.
4. The method as claimed in any one of the preceding claims, wherein said second reactive gas has fluorine atoms associated therewith, with each of said first and second reactive gases being introduced into said processing chamber along with a carrier gas, and wherein the method further includes controlling a quantity of said fluorine atoms associated with said nucleation layer as a function of said carrier gas.
5. The method as claimed in any one of the preceding claims, wherein forming atop of said nucleation layer includes forming said bulk deposition layer employing chemical vapor deposition.
6. The method as claimed in any one of claims 1 to 4, wherein forming atop of said nucleation layer includes forming said bulk deposition layer employing physical vapor deposition.
7. The method as claimed in any one of the preceding claims, wherein forming a nucleation layer further includes introducing said first and second gases therein so as to purge said processing chamber of said first reactive gas by introducing a purge gas therein, before exposing said substrate to said second reactive gas.
8. The method as claimed in any one of claims 1 to 6, wherein forming a nucleation layer further includes purging said processing chamber of said first reactive gas by pumping said processing chamber clear of all gases disposed therein before introducing said second reactive gas.
9. The method as claimed in any one of claims 1 to 6,

wherein forming a nucleation layer further includes purging said processing chamber of said first reactive gas by introducing a purge gas subsequently pumping said processing chamber clear of all gases disposed therein before exposing said substrate to said second reactive gas.

10. The method as claimed in any one of the preceding claims, wherein forming a nucleation layer includes forming alternating layers of a hydrogen containing compound and a refractory metal.

11. A processing system for a substrate, said system comprising:

a body defining a processing chamber;
 a holder, disposed within said processing chamber, to support, in use, a substrate;
 a gas delivery system in fluid communication with said processing chamber;
 a temperature control system in thermal communication with said processing chamber;
 a pressure control system in fluid communication with said processing chamber;
 a controller in electrical communication with said gas delivery system, said temperature control system, and said pressure control system; and
 a memory in data communication with said controller, said memory comprising a computer-readable medium having a computer-readable program embodied therein, said computer-readable program including a first set of instructions for controlling said gas delivery system to form, in use, a nucleation layer by serially exposing said substrate to first and second reactive gases, and a second set of instructions to control said gas delivery system to form, in use, top of said nucleation layer, a bulk deposition layer by subjecting said nucleation layer to vapor deposition of a compound contained in one of said first and second reactive gases.

12. The processing system as claimed in claim 11 further including:

an additional body defining an additional processing chamber;
 an additional holder, disposed within said additional processing chamber, to support, in use, a substrate;
 an additional temperature control system in thermal communication with said second processing chamber;
 an additional pressure control system in fluid communication with said additional processing chamber; and
 a robotic handler disposed between said first

processing chamber and said additional processing chamber, with said gas delivery system being in fluid communication with said additional processing chamber, and said controller being in electrical communication with said additional temperature control system, said additional pressure control system and said robotic handler;

wherein said first set of instructions further includes a first sub-routine to control said gas delivery system to form, in use, said nucleation layer while said substrate is in said processing chamber, and wherein said second set of instructions further includes a second sub-routine to control said robotic handler to move, in use, said substrate between said processing chamber and said additional processing chamber and control said gas delivery system to form said bulk deposition layer while said substrate is disposed in said additional processing chamber.

13. The processing system as claimed in claim 12, wherein said second reactive gas has fluorine atoms associated therewith, and wherein said first set of instructions further includes a sub-routine to introduce each of said first and second reactive gases into said processing chamber along with a carrier gas, and wherein said computer-readable program further includes a third set of instructions to control a quantity of said fluorine atoms associated with the nucleation layer as a function of said carrier gas.

14. The processing system as claimed in claim 13, wherein said computer-readable program includes an additional set of instructions to purge said first processing chamber of said first reactive gas before introducing said second reactive gas by introducing a purge gas therein.

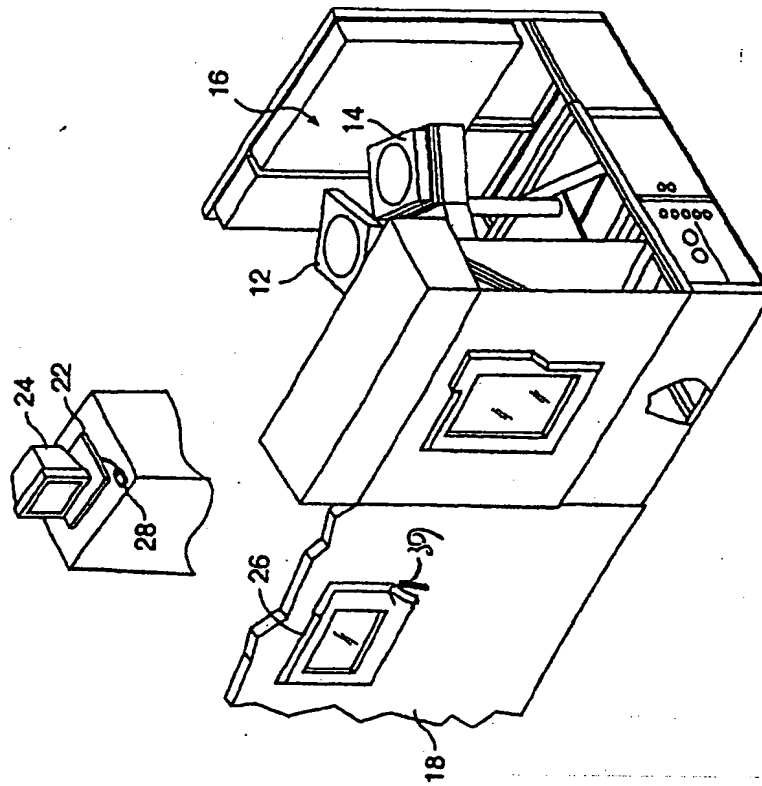


FIG. 1

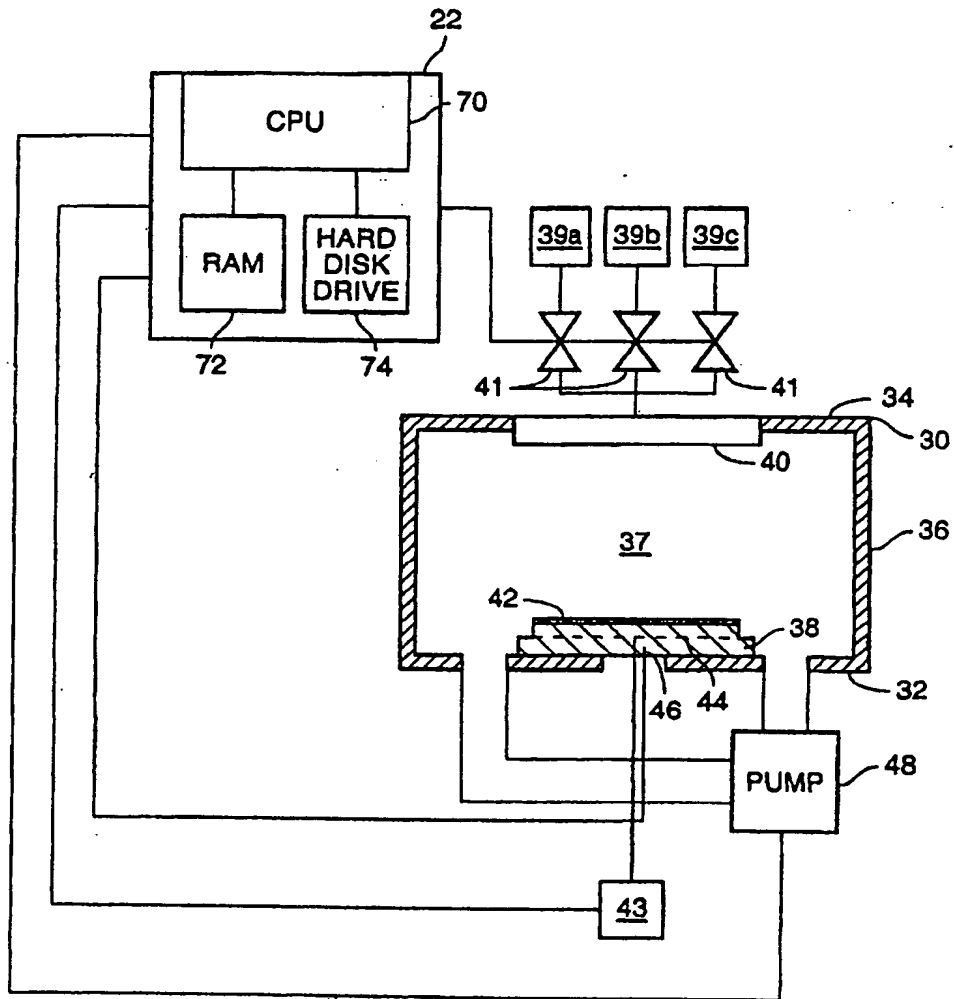


FIG. 2

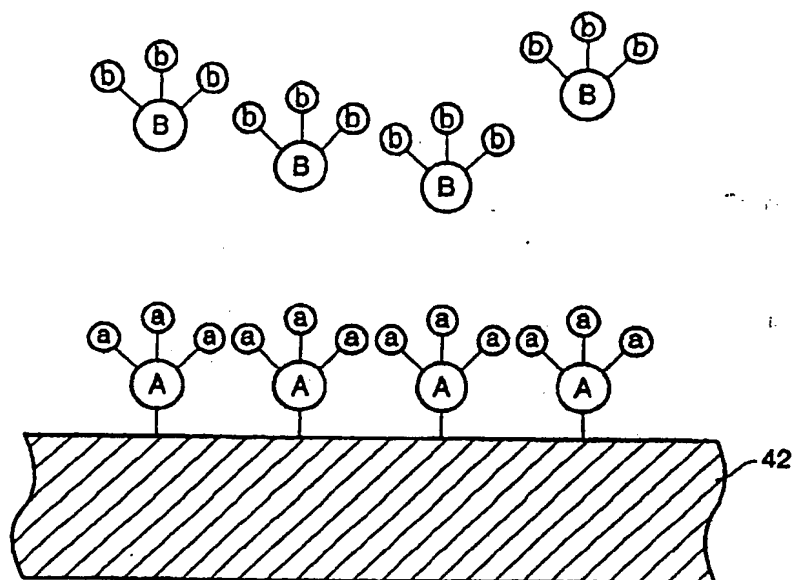


FIG. 3

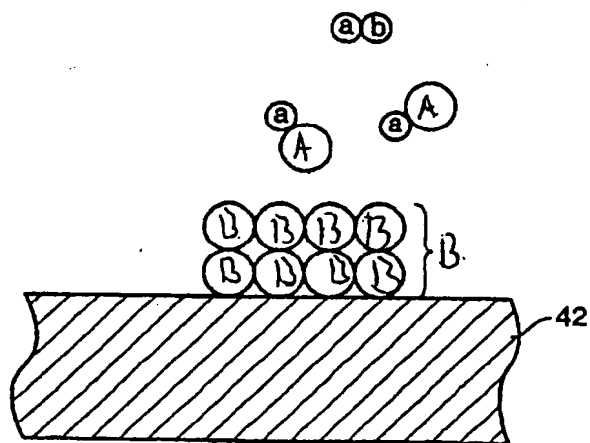
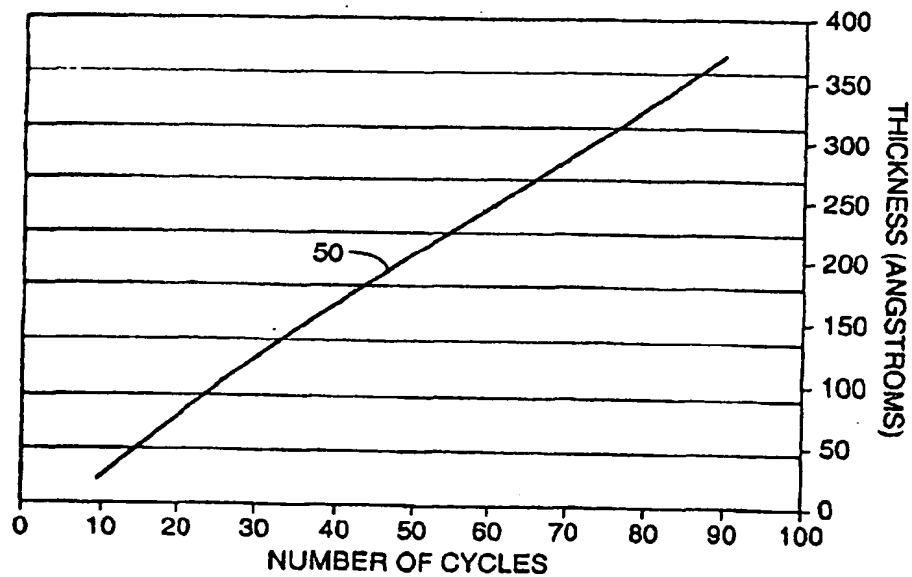
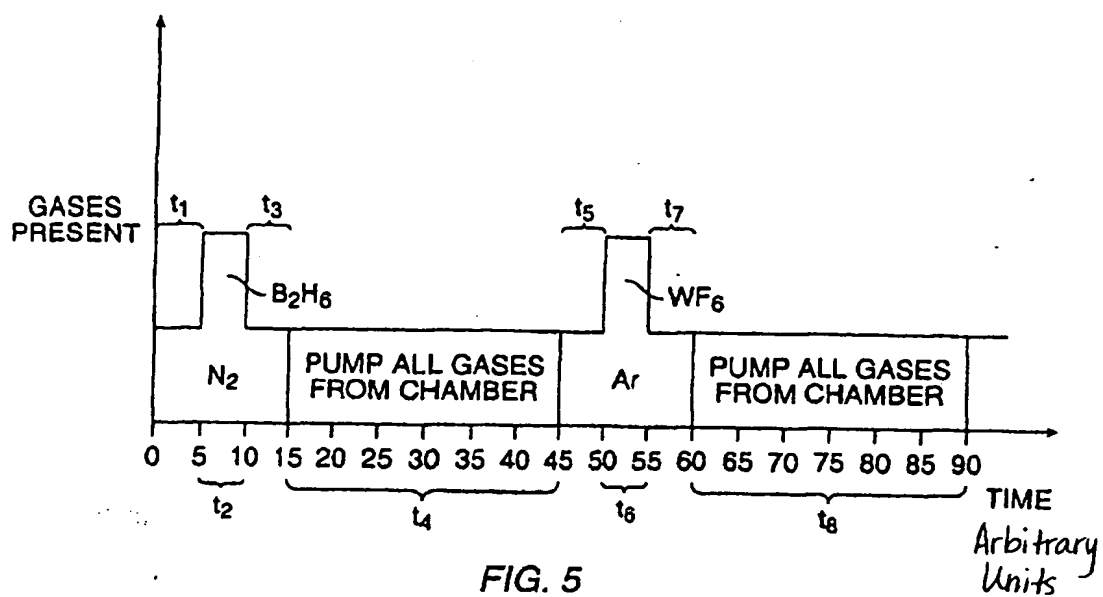


FIG. 4



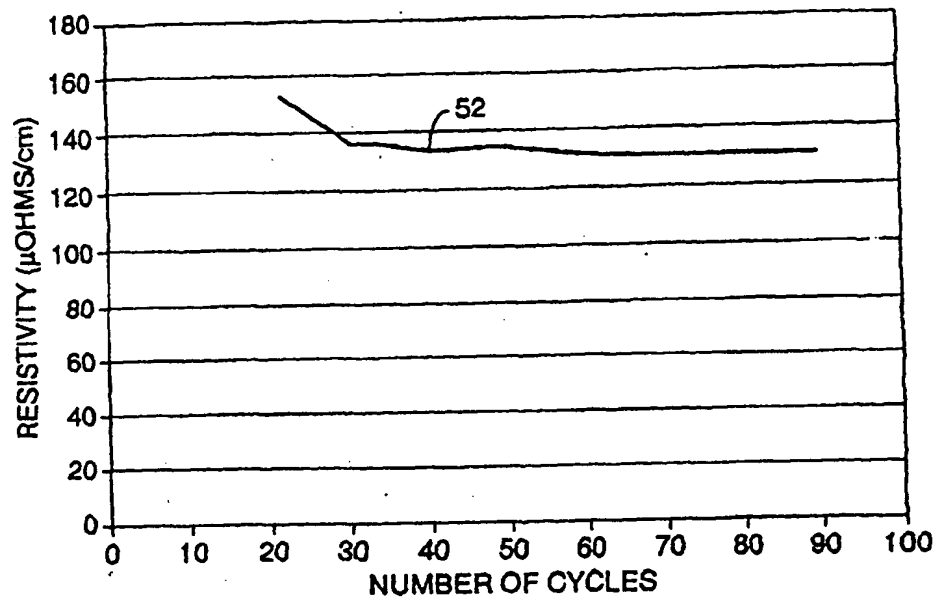


FIG. 7

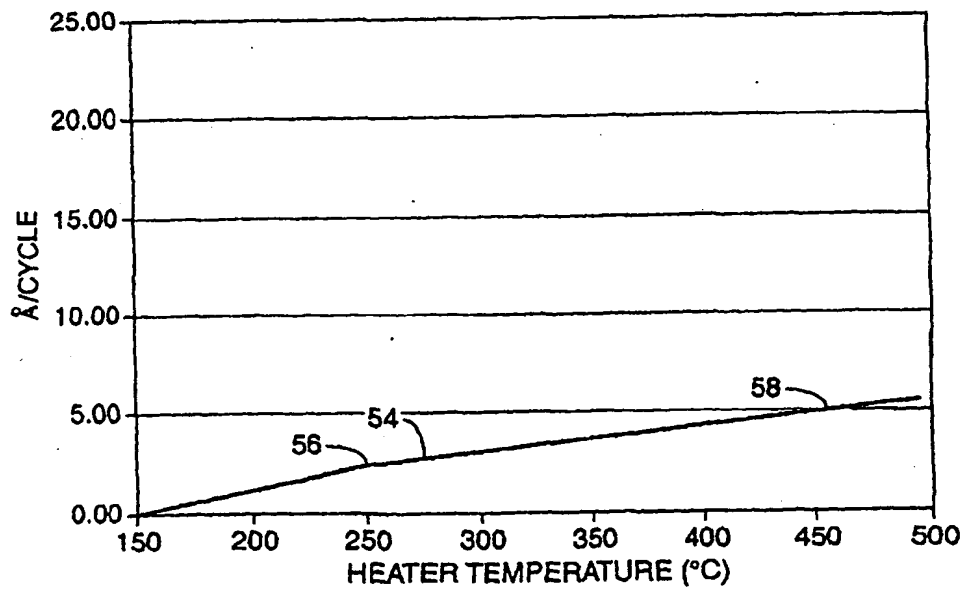


FIG. 8

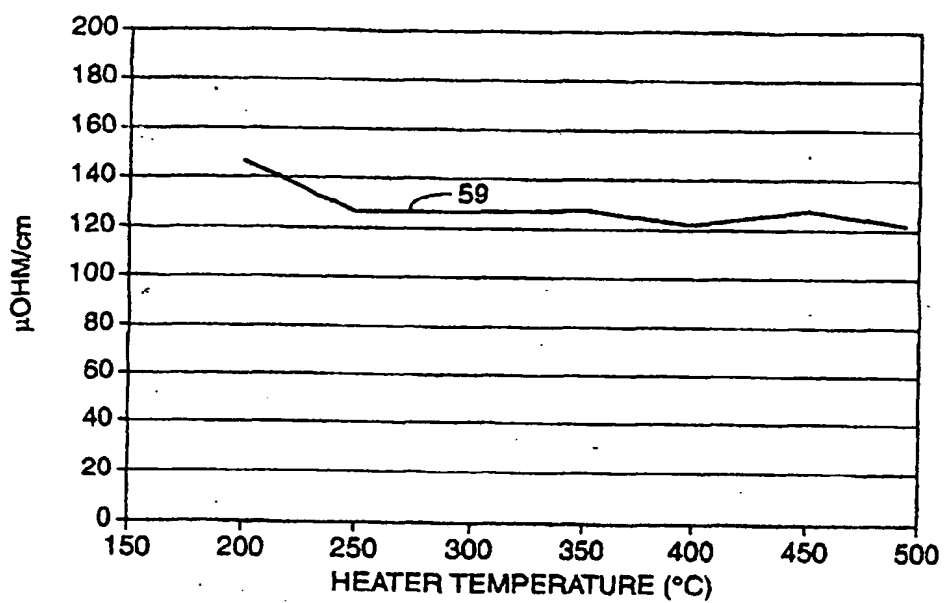


FIG. 9

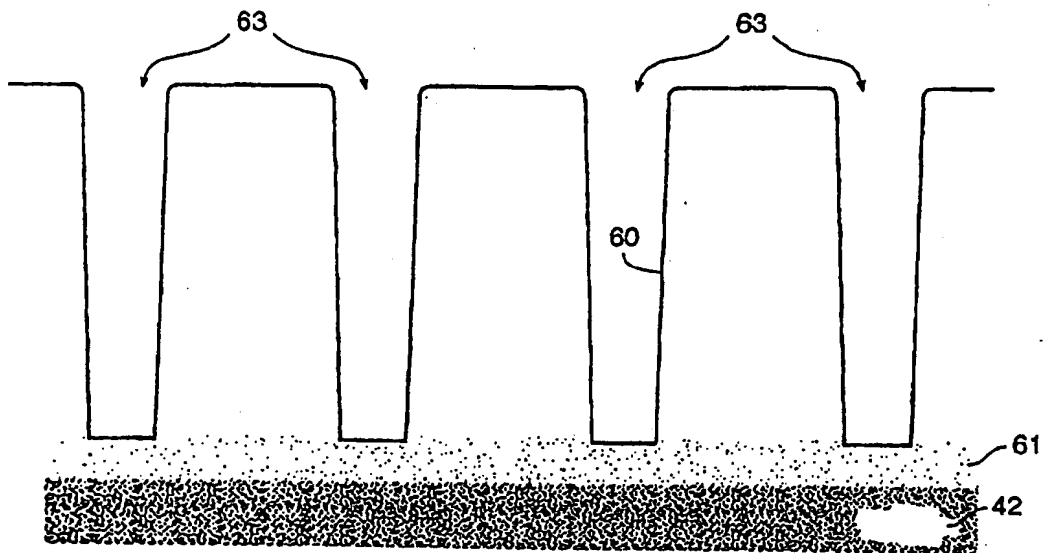


FIG. 10

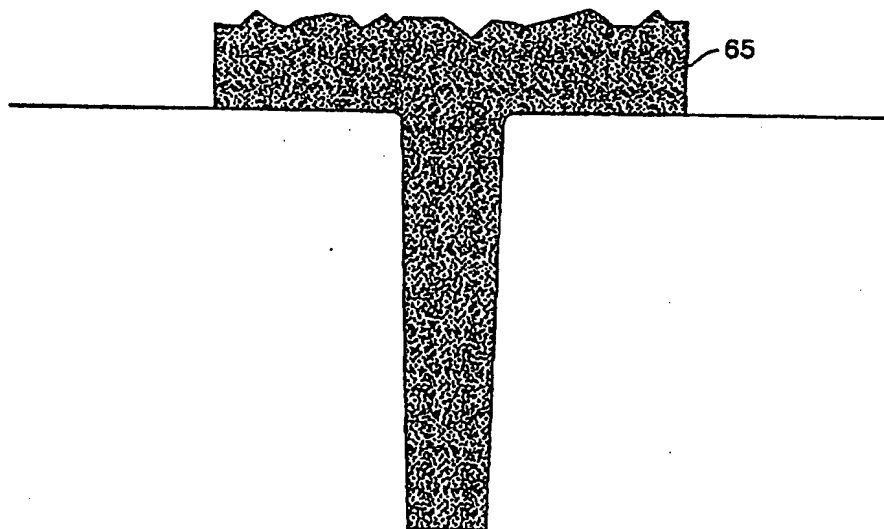
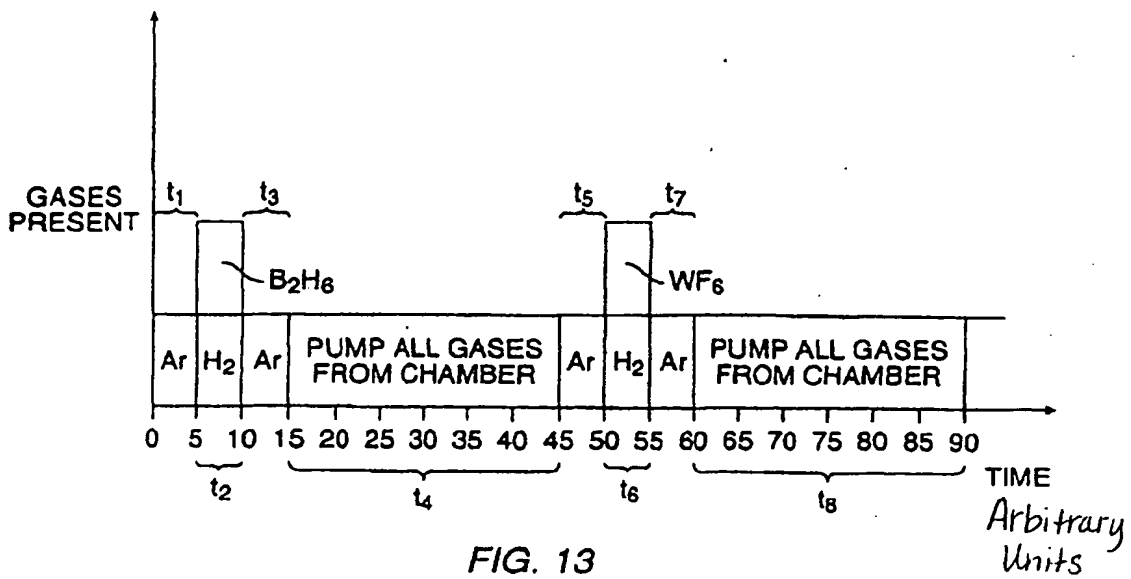
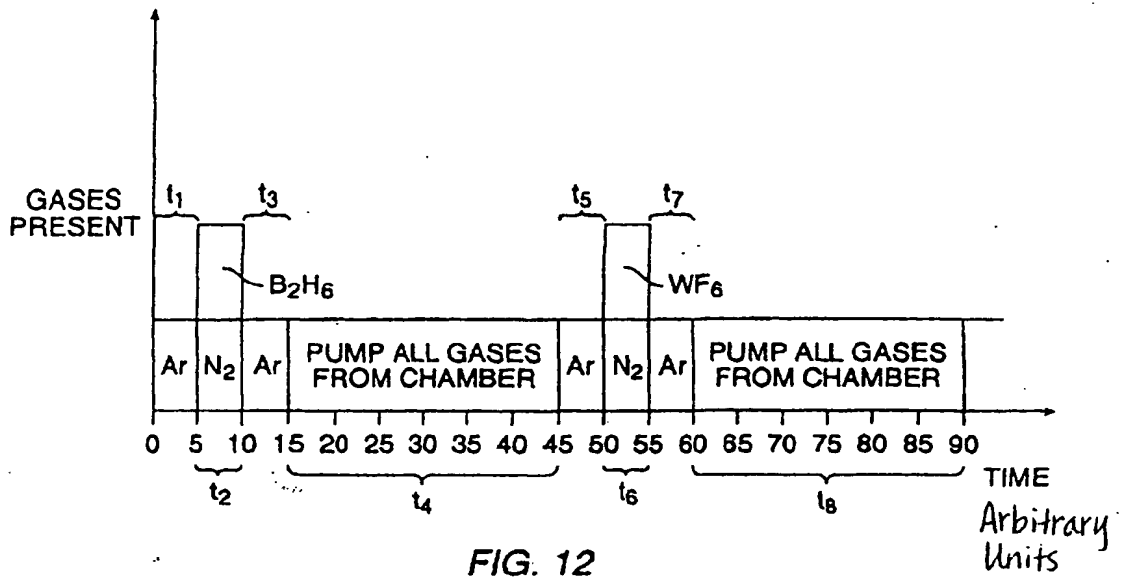


FIG. 11



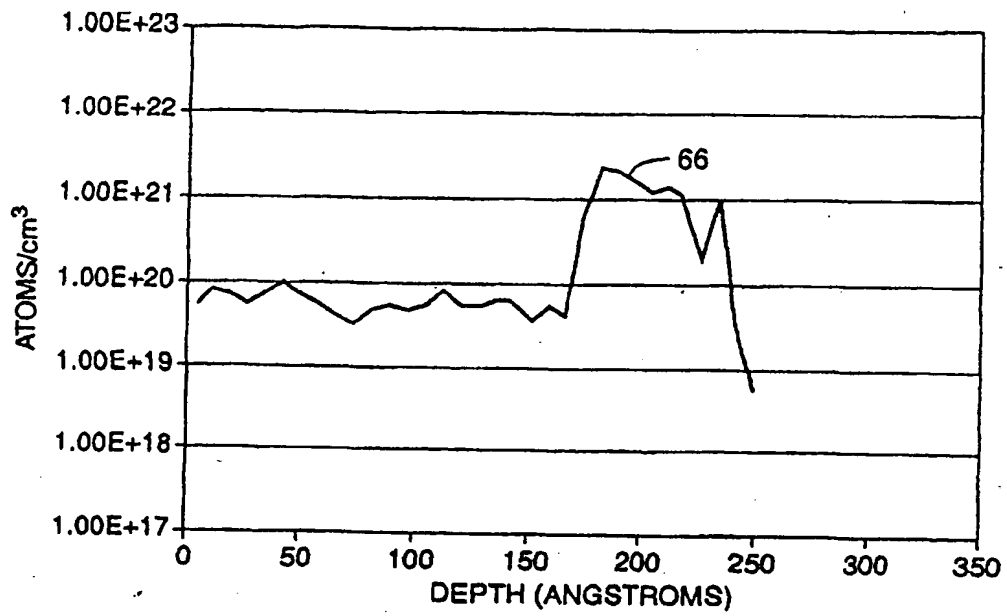


FIG. 14

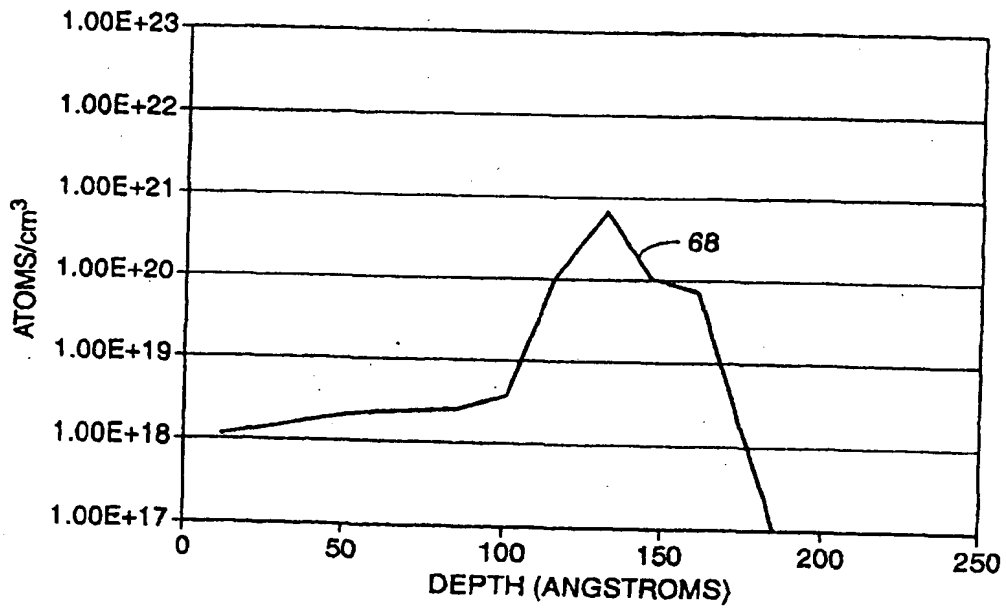


FIG. 15



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 4779

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	WO 98 51838 A (MAEDA YUJI ;OHTSUKA KEIICHI (JP); YAMAZAKI MANABU (JP); APPLIED MA) 19 November 1998 (1998-11-19)	1-3,5,7,9-12,14	C23C16/02
A	* page 11, line 20 - page 13, line 9 * * claims 17,18 *	4,6,8,13	
X	US 5 580 380 A (MCCLURE MICHAEL T ET AL) 3 December 1996 (1996-12-03) * column 6, line 50 - column 7, line 21 * * column 8, line 26-59 *	1,2,5	
The present search report has been drawn up for all claims			<p>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</p> <p>C23C C30B</p>
Place of search THE HAGUE		Date of completion of the search 5 October 2001	Examiner Castagné, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03/92 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 4779

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-10-2001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9851838 A	19-11-1998	US 6156382 A	05-12-2000
		AU 7575598 A	08-12-1998
		EP 0981656 A1	01-03-2000
		WO 9851838 A1	19-11-1998
US 5580380 A	03-12-1996	US 5397428 A	14-03-1995
		AU 3416993 A	28-07-1993
		CA 2125873 A1	08-07-1993
		DE 69208480 D1	28-03-1996
		DE 69208480 T2	14-11-1996
		EP 0617741 A1	05-10-1994
		JP 2648394 B2	27-08-1997
		JP 7506799 T	27-07-1995
		KR 170441 B1	18-02-1999
		US 5420443 A	30-05-1995
		WO 9313242 A1	08-07-1993
		US 5458733 A	17-10-1995
		US 5562769 A	08-10-1996

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82